Date Submitted: [09/02/2016]

Air Liquide

Location of Headquarters: Houston, TX, USA
Location of Biofuel Production Facility: Application is for a generic pathway, but references current Air Liquide production facilities:

- Conley, GA (biogas production facility) - "Live Oak"
- Rodeo, CA (hydrogen production facility) - "Rodeo SMR"

Fuel Pathway Requested

Fuel Type	Feedstock	Production Process Technology	RIN D-Code Requested
Hydrogen	**Biogas** from landfills, municipal wastewater treatment facility digesters, agricultural digesters, and separated MSW digesters	**Steam Methane Reforming (SMR)**	**3**

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A. Technical Justification

1. Fuel Pathway Description

Air Liquide petitions the Agency under the Renewable Fuels Standard (RFS) program to generate D3 RINs (cellulosic) for renewable hydrogen made from waste-derived biogas. Air Liquide’s biogas-to-hydrogen process uses waste-derived biogas from landfills, municipal wastewater treatment facility digesters, agricultural digesters, and separated MSW digesters to produce hydrogen by:

1. Upgrading the collected biogas to renewable natural gas via membrane separation (an in-house Air Liquide technology)
2. Injecting renewable natural gas into a commercial distribution system (common carrier pipeline)
3. Taking equal quantity of gas from the common carrier pipeline connected to a hydrogen production unit (steam methane reformer or “SMR”). The SMR process uses electricity from the grid along with steam to produce synthesis gas (“syngas”) which is then purified to fuel cell quality hydrogen via pressure swing absorption (PSA).
4. Compressing and transporting the purified hydrogen via high pressure tube trailer to a hydrogen refueling station (HRS). In the case of a small SMR located onsite at a hydrogen refueling station, the transport via tube trailer is not needed.
5. Dispensing corresponding amount of renewable hydrogen at the HRS for use in small/medium-duty hydrogen fuel cell electric vehicles (HFCEVs).

EPA previously evaluated biogas production from landfills in the final rule published on March 26, 2010 (75 FR 14760) (the “March 2010 RFS rule”) and modeled in more detail the suite of biogas from landfills, separated MSW digesters, wastewater treatment digesters, agricultural digesters, and other waste digesters (“waste-derived biogas”) as a feedstock for biofuel production in the final rule published on July 18, 2014 (79 FR 42128) (the “July 2014 RFS rule”).

Today the SMR process is widely used for the production of hydrogen for industrial applications. By replacing the fossil natural gas feed in the SMR process with renewable natural gas (RNG) from upgraded waste-derived biogas, the process produces a renewable hydrogen product. The pathway will use a mass balance approach where only a portion of the natural gas feedstock associated with vehicle fuel will be based on RNG via pipeline injection. The renewable hydrogen produced through Air Liquide’s biogas-to-hydrogen process is intended for use in the transportation sector, specifically for light/medium duty hydrogen fuel cell electric vehicles (HFCEV). Hydrogen product at the SMR plant will be compressed and transported via high pressure tube trailers to hydrogen fueling stations in surrounding areas. In the case of a small onsite SMR located at the refueling station, no transport is needed.

2. Process Flow Charts

Figure 1: *Biogas-to-hydrogen flow chart (centralized SMR)*

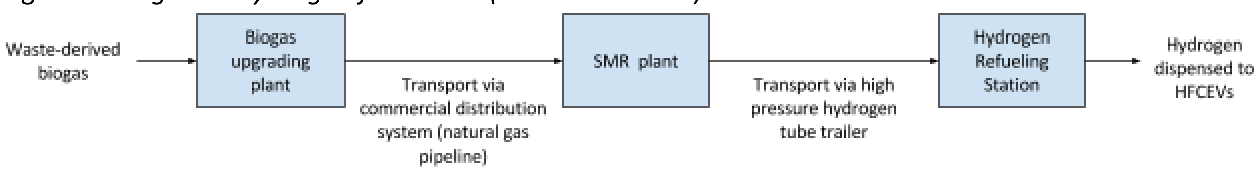


Figure 2: *Biogas-to-hydrogen flow chart (onsite SMR)*

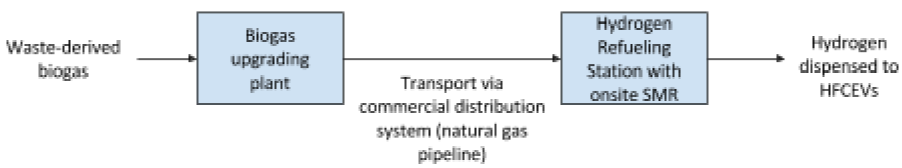


Figure 3: *Biogas upgrading plant block flow diagram*

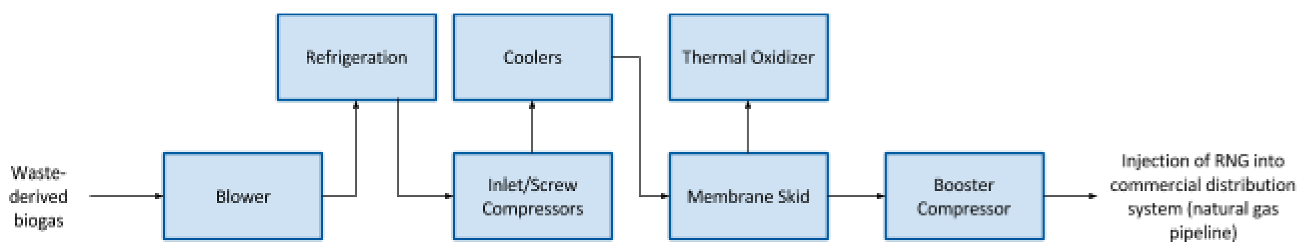
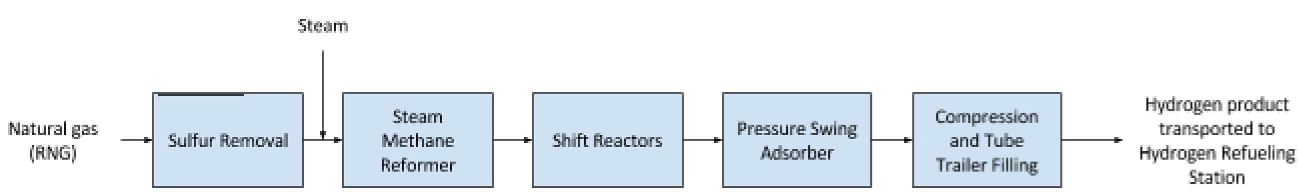


Figure 4: *Steam methane reforming plant block flow diagram*



3. Comparison to Previously Evaluated Pathways

There are currently no approved pathways for renewable hydrogen generation in the RFS program. However, the proposed biogas-to-hydrogen pathway can be compared to pathway ‘Q’ under the current RFS program, which defines renewable compressed natural gas (CNG) and renewable liquefied natural gas (LNG) from feedstock which includes biogas from landfills, municipal wastewater treatment facility digesters, agricultural digesters, and separated MSW digesters; and biogas from the cellulosic components of biomass processed in other waste digesters (eCFR §80.1426 Table 1)[1]. This pathway currently generates D3 RINs. The proposed biogas-to-hydrogen pathway utilizes the same feedstock and further processes the renewable natural gas into renewable hydrogen through steam methane reforming.

Similarities between the two pathways also exist in feedstock accounting mechanisms and tracking/record keeping of renewable natural gas from the point of injection into the commercial distribution system to where the fuel is dispensed at the fueling station for use in HFCEVs. In the proposed biogas-to-hydrogen pathway, the renewable natural gas from the biogas upgrading plant is transported to the SMR plant via a commercial distribution system. Once the renewable natural gas is processed into hydrogen (stoichiometrically, two hydrogen molecules are produced from one methane molecule), the product is compressed and transported by high pressure tube trailers to the refueling station (in the case of a centralized SMR). The renewable hydrogen dispensed at the hydrogen refueling station corresponds to the relative amount of renewable natural gas used to produce the fuel. The amount of renewable natural gas injected into the commercial distribution system is tracked and reported along with the amount of fuel dispensed at the hydrogen fueling station to ensure correct allocation and renewable classification. This tracking and reporting mechanism is similar to that which is practiced in the renewable CNG/LNG pathways and would be subject to comparable record keeping as defined in §80.1454 (k)(1).

Similar rules around RIN generation, as defined in eCFR §80.1426(f)(11)(ii) for the renewable CNG/LNG pathway, will also apply to the proposed biogas-to-hydrogen pathway. Among these, it will be ensured that renewable natural gas used to produce renewable hydrogen will only generate RINs for the corresponding amount of hydrogen fuel produced. No other party will rely on the volume of biogas/CNG/LNG for the creation of RINs. Additional rules for RIN generation will apply as well, and will be comparable to those of the renewable CNG/LNG pathway.

The proposed biogas-to-hydrogen pathway would also be subject to similar registration requirements under the RFS program as defined in §80.1450(b)(1)(v)(D), which applies to facilities producing other renewable fuel from biogas.

Comparable to the renewable CNG/LNG pathway, a mass-balance approach is proposed for the production of renewable hydrogen at the SMR. In this approach, the amount of renewable natural gas injected into the commercial distribution system at the biogas upgrading plant corresponds to an equal amount of natural gas withdrawn from the pipeline at the SMR plant that is processed into a relative amount of renewable hydrogen for use in HFCEVs. In the case of a large, centralized SMR, the plant produces hydrogen predominantly for industrial use. Production of hydrogen at these facilities for use in the HFCEV market will continue to ramp up as the market grows. However for now, it is only a small portion of the entire hydrogen output from the plant. Thus for the time being, Air Liquide will consider all renewable natural gas withdrawn from the pipeline at the SMR to be processed into renewable hydrogen for transportation. The remaining hydrogen produced for industrial applications will continue to be processed from fossil natural gas withdrawn from the pipeline.

In addition to the above comparisons in the current RFS program, the California Low Carbon Fuel Standards (LCFS) has identified 11 hydrogen pathways, including five that utilize steam methane reforming as the primary production process. Variances in the pathways include onsite vs. centralized reforming, hydrogen compression vs. liquefaction, and use of fossil natural gas vs. renewable feedstocks.

4. Commercial Viability

Production of hydrogen via steam methane reforming using renewable natural gas (RNG) as feedstock is one of the most economical processes currently available to produce renewable hydrogen. Steam methane reforming is the most widely-used and efficient process for hydrogen production, supplying 95% of today’s hydrogen generated from fossil natural gas. The proposed biogas to hydrogen pathway via steam methane reformation of RNG builds on this established process and utilizes existing SMR plant infrastructure and interstate natural gas pipeline for feedstock transportation, thus eliminating the need for expensive capital investment in new plants and infrastructure.

5. Renewable Fuel Production Volumes (Historic and Projected)

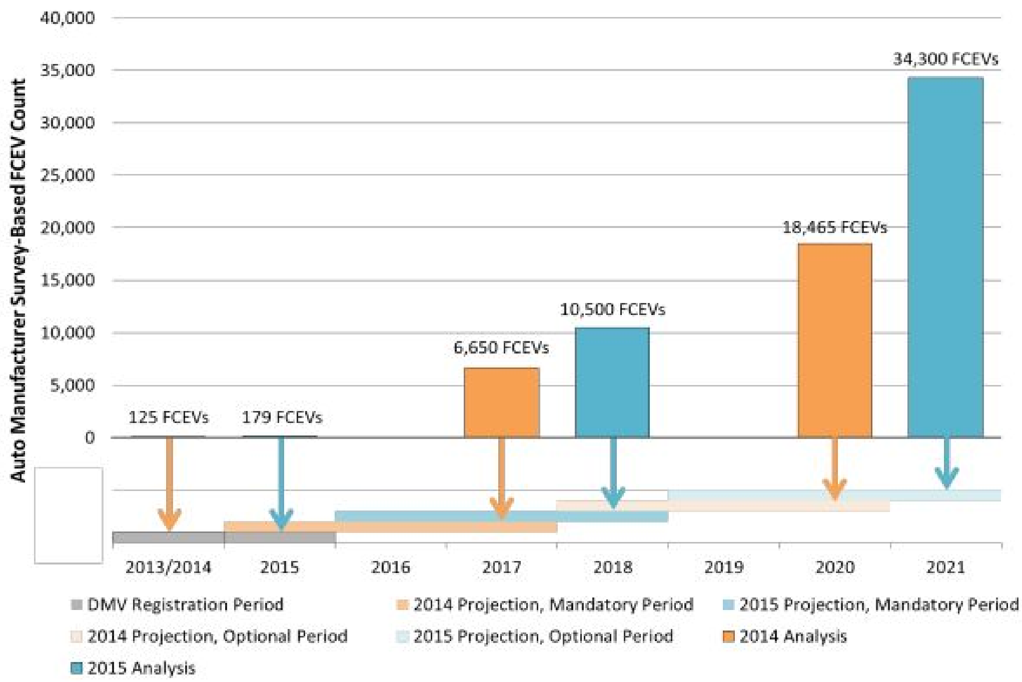
Air Liquide has not yet produced renewable hydrogen under the proposed biogas-to-hydrogen pathway. However, Air Liquide has extensive experience in producing both renewable natural gas and hydrogen. Though the proposed pathway is intended to be applied as a generic biogas-to-hydrogen pathway, Air Liquide will provide operational data from existing plants to illustrate the overall production process.

The two facilities of reference are the Live Oak biogas production facility in Conley, GA (“ Live Oak”) and the SMR facility in Rodeo, California (“Rodeo SMR”). Both plants have been in operation since 2009. *[*(b) (4) [redacted]*.]* With extensive experience in both biogas upgrading and hydrogen production, Air Liquide is well-qualified and prepared to link the two production processes in the proposed biogas-to-hydrogen pathway.

Furthermore, Air Liquide is committed to advancing the “Hydrogen Economy” globally, with special focus on mobility applications. The company has already invested or has planned investment in hydrogen refueling infrastructure in California, the northeast United States, and other countries (France, Germany, Japan, Denmark). To date, more than 75 hydrogen fueling stations have been designed and installed by Air Liquide worldwide. For the US stations, hydrogen is or will be supplied by large central SMRs such as the Rodeo SMR or small on-site SMR units (located at the station). As the HFCEV demand increases, the demand for renewable fuel can be met by displacing the corresponding amount of natural gas used as feed to the central/onsite SMRs with RNG from landfills, wastewater treatment facilities, and anaerobic digesters.

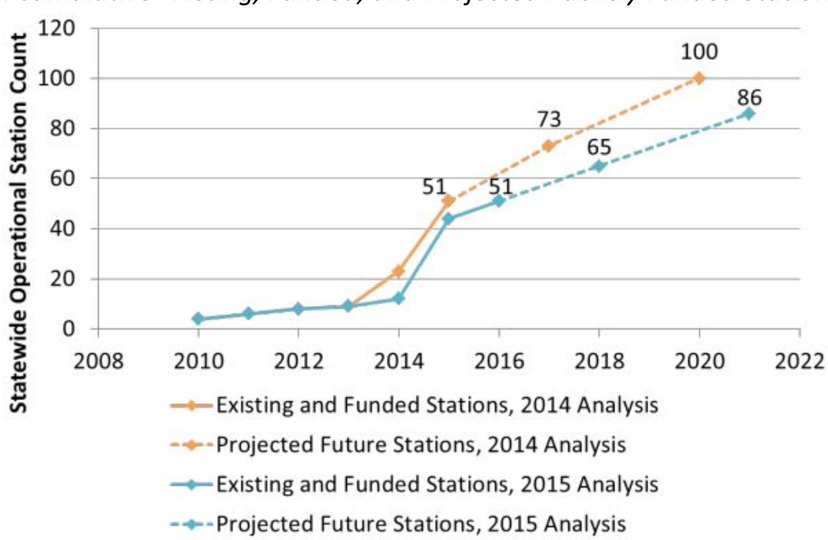
The state of California leads the way in hydrogen infrastructure development and vehicle adoption. As shown in Figure 5, the California Air Resources Board (ARB) predicts that California HFCEV fleet will grow to 10,500 by the end of 2018 and 34,300 by the end of 2021. Furthermore, ARB projects 51 currently funded and operational stations will be available by the end of 2016, as shown in Figure 6. These 51 stations will have a fueling capacity of 9,400 kilograms per day, equivalent to an expected demand of approximately 13,500 HFCEVs.[3]

Figure 5: *Current and Projected On-Road FCEV Populations*



Source: "2015 Annual Evaluation of Fuel Cell Electric Vehicle Deployment and Hydrogen Fuel Station Network Development", CARB

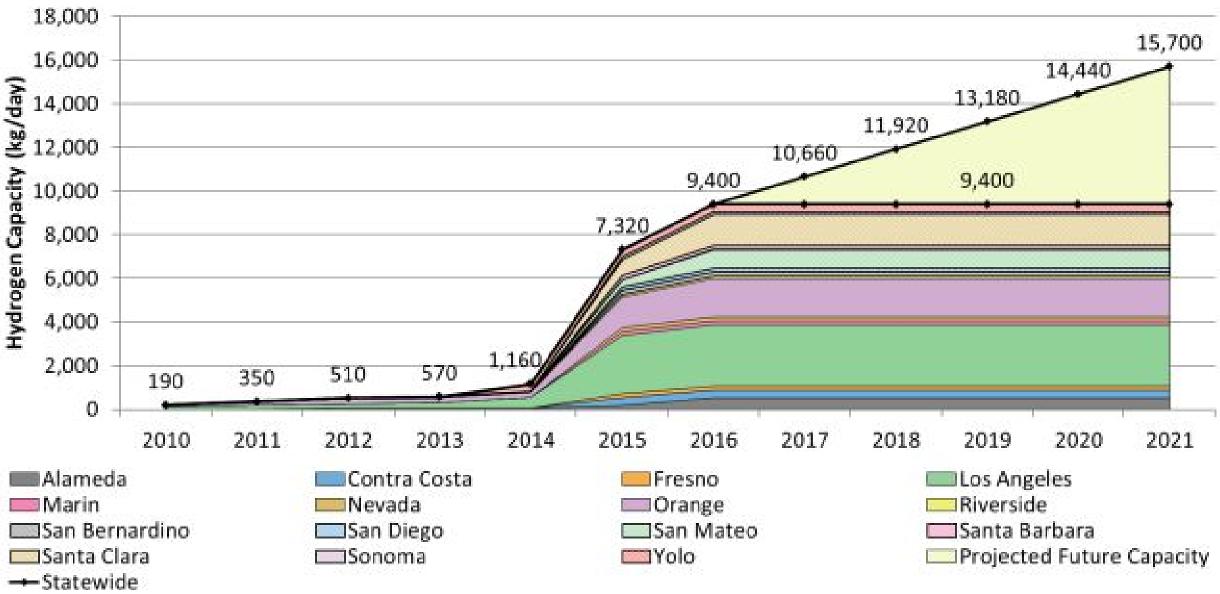
Figure 6: *Cumulative Existing, Funded, and Projected Publicly Funded Station Counts*



Source: "2015 Annual Evaluation of Fuel Cell Electric Vehicle Deployment and Hydrogen Fuel Station Network Development", CARB

The projections for number of FCEVs on the road and hydrogen refueling stations available in California correspond to projections for hydrogen fuel demand. Figure 7 shows projected hydrogen capacity reaching 15,700 kg/day by 2021 for the state of California.[3]

Figure 7: *Statewide and By County Hydrogen Fueling Capacity*



Source: "2015 Annual Evaluation of Fuel Cell Electric Vehicle Deployment and Hydrogen Fuel Station Network Development" (CARB)

Along with the growth of the hydrogen mobility market in California, additional growth is projected for the northeastern region of United States. This growth is driven by a collaboration between Air Liquide and Toyota Motor Sales USA to build twelve hydrogen refueling stations in the northeast U.S., with the first stations slated to open to the public by early 2017.

B. Organization Information

1. Organization Description

World leader in gases, technologies and services for Industry and Health, Air Liquide is present in 80 countries with more than 50,000 employees and serves more than two million customers and patients. Oxygen, nitrogen and hydrogen have been at the core of the company's activities since its creation in 1902. Air Liquide's ambition is to be the leader in its industry, delivering long-term performance and acting responsibly.

Air Liquide Advanced Technologies (ALAT) specializes in gas engineering and cryogenics and operates in business sectors as varied and specialized as Aeronautics, Space, Marine, Scientific Research, Hydrogen energy, but also Chemicals and Pharmaceuticals, Electronics and Optoelectronics. Air Liquide is actively involved in setting up the hydrogen energy industry at global level. The Group has delivered more than 60 hydrogen stations worldwide. Air Liquide already operates hydrogen filling stations for the general public in Europe, including Rotterdam, Netherlands and Düsseldorf, Germany. In Germany, Air Liquide is also a partner of the "H2 Mobility initiative" which aims to deploy about 400 hydrogen stations covering the whole country by 2023. In 2014, the Group announced the installation of four new hydrogen filling stations in Denmark (the first hydrogen infrastructure network in Europe at national level).

Air Liquide Advanced Technologies U.S. LLC is the U.S. division of ALAT that includes the Biogas and Hydrogen Energy teams. In 2014, Air Liquide announced plans to develop and supply a fully-integrated hydrogen fueling infrastructure in the northeast United States, in collaboration with Toyota Motor Sales USA, Inc. (Toyota), to support Toyota's introduction of a new hydrogen fuel cell electric vehicle (HFCEV), the "Mirai", and its plans to deliver hydrogen FCEVs in the United States. Air Liquide's U.S. hydrogen fueling infrastructure in the northeast will initially consist of twelve filling stations across a number of states, with plans to extend the network as demand warrants. Air Liquide is also working to open hydrogen fueling stations in California.

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C. Fuel Type

1. Technical Description

Hydrogen is used as fuel in hydrogen fuel cell electric vehicles (HFCEV) which produce zero CO_2 emissions at the tailpipe. A number of automotive manufacturers have already developed or are in the process of developing HFCEV models, including Toyota, Hyundai, Mercedes-Benz, BMW, and Honda. These vehicles use a Proton Exchange Membrane (PEM) fuel cell to convert gaseous hydrogen and oxygen into electric energy and water. The vehicle's hydrogen tank holds approximately 5 kg (2.268 lb) of hydrogen, which will power the vehicle for around 300 miles.

Hydrogen is best suited for light/medium duty vehicles, but can also be used in larger vehicles such as buses, and smaller applications such as bikes, scooters, and forklifts. However, Air Liquide's proposed pathway focuses on hydrogen fuel for light/medium duty vehicles, such as the Toyota Mirai.

2. Information for New Fuel Types

i. Chemical Composition

The hydrogen diatomic molecule consists of two hydrogen atoms (H_2). The lower heating value of hydrogen i s 120.21 MJ/kg (51,682 Btu (LHV)/lb)[2] .

ii. Regulatory Definition Justification

Renewable hydrogen produced via steam methane reforming using renewable natural gas upgraded from waste-derived biogas is expected to qualify for D3 RINs given the cellulosic classification of the feedstock, waste-derived biogas.

iii. Equivalence Value Application

The standard EV calculation is designed for an internal combustion (IC) engine. As such, it does not adequately reflect the different drivetrain of HFCEVs. Therefore, **Air Liquide proposes an adjusted equivalence value (EV) value for the biogas-to-hydrogen pathway, where 0.58 lb (.263 kg) H_2 represents one gallon of renewable fuel with an EV of 1.0.** This value is obtained using the standard calculation for EV and an EER multiplier term of 2.5 to adjust for higher fuel economy in light/medium duty HFCEVs. The approach is similar to that of the California Air Resources Board (CARB).

An "Energy Economy Ratio" (EER) is a dimensionless value that represents the efficiency of a fuel used in a powertrain as compared to a reference fuel. EERs are typically a comparison of miles per gasoline gallon equivalent (mpge) between two fuels. CARB has defined EER terms in the state's Low Carbon Fuel Standards (LCFS) for a number of alternative fuels, as shown in the table below. For light/medium duty hydrogen fuel cell vehicles, the EER value relative to gasoline is 2.5. *Note: this application only focuses on light-medium duty applications. Heavy-duty/off-road applications can be addressed at a later time.

Table 1: EER Values for Fuels Used in Light- and Medium-Duty, and Heavy-Duty Applications

Light/Medium-Duty Applications (Fuels used as gasoline replacement)		***Heavy-Duty/Off-Road Applications (Fuels used as diesel replacement)***	
Fuel/Vehicle Combination	***EER Values Relative to Gasoline***	***Fuel/Vehicle Combination***	***EER Values Relative to Diesel***
Gasoline (incl. E6 and E10) or E85 (and other ethanol blends)	1.0	Diesel fuel or Biomass-based diesel blends	1.0
CNG/ICEV	1.0	CNG or LNG (Spark-Ignition Engines)	0.9
		CNG or LNG (Compression-Ignition Engines)	1.0
Electricity/BEV, or PHEV	3.4	Electricity/BEV, or PHEV* Truck	2.7
		Electricity/BEV or PHEV* Bus	4.2
		Electricity/Fixed Guideway, Heavy Rail	4.6
		Electricity/Fixed Guideway, Light Rail	3.3
		Electricity/Trolley Bus, Cable Car, Street Car	3.1
		Electricity Forklifts	3.8
H2/FCV	2.5	H2/FCV	1.9
		H2 Fuel Cell Forklifts	2.1

*BEV = battery electric vehicle, PHEV= plug-in hybrid electric vehicle, FCV = fuel cell vehicle, ICEV = internal combustion engine vehicle.

Source: http://www.arb.ca.gov/regact/2015/lcfs2015/lcfsfinalregorder.pdf

As seen in the table above, EER values for gasoline, diesel, and CNG/LNG vehicles are 1.0. Subsequently, the EVs that have been calculated for these fuels and their replacement renewable fuels under eCFR §80.1415 would remain unchanged by the proposed use of the EER multiplier term.

Along with adequately reflecting the different drivetrain of HFCEVs, the adjusted EV will help to encourage renewable hydrogen production from renewable natural gas. In the proposed biogas-to-hydrogen pathway, the feedstock (renewable natural gas) for the final process (steam methane reforming) is a feedstock only needing compression or liquefaction to become a renewable fuel (CNG/LNG) defined under the Renewable Fuel Standard (RFS). In the absence of an EER multiplier, there is no incentive for renewable natural gas producers to further process the fuel into renewable hydrogen, rather than CNG/LNG. Additionally, calculating EV based only on energy content ignores the greatest advantage of HFCEV: that vehicles with this drivetrain go a much farther distance on the same amount of energy than a typical IC engine vehicle. This advantage is factored in with the EER approach and accounts for the equivalent displacement of gasoline vehicles on the road.

To reflect the different drive train of hydrogen fuel cell vehicles and overcome the disadvantage of producing renewable hydrogen over renewable natural gas from the same feedstock, Air Liquide proposes to use the EER value of 2.5 as a multiplier in the EV equation for the biogas-to-hydrogen pathway. This would result in 0.58 lbs (.263 kg) of H_2 representing one gallon of renewable fuel with an EV of 1.0. The 0.58 value is obtained by back-calculating from an EV of 1.0 with the 2.5 EER term included the original equation. The lower heating value (LHV) of 51,682 BTU is used to represent the energy content of H_2.[2]

$$EV = (.58\ lb\ H_2)\ \left(\frac{1}{0.972}\right) \times \left(\frac{51{,}682\ BTU\ (LHV)}{77{,}000}\right) \times (2.5) = 1.0$$

iv. Fuel Registration

It is not necessary for a hydrogen producer to register under 40 CFR Part 79 because hydrogen is considered an alternative fuel.

There are, however, published hydrogen fuel quality standards which would apply to the biogas-to-hydrogen pathway. SAE International has published hydrogen fuel quality standards (J2719) for commercial proton exchange membrane (PEM) fuel cell vehicles. The purpose of this hydrogen fuel quality standard is to specify hydrogen fuel quality requirements for all commercial hydrogen fueling stations for PEM fuel cell vehicles (FCVs). Hydrogen quality is defined as the quality measured at the dispenser nozzle using a suitable adapter and methodology developed by the ASTM D03 (Gaseous Fuels) Committee.[4]

3. Other Relevant Information

N/A

D. Production Process

1. Steam Methane Reforming

Process Overview

Air Liquide’s biogas-to-hydrogen process utilizes waste-derived biogas to produce hydrogen by: 1) upgrading the collected biogas to RNG via membrane separation 2) injecting and transporting RNG via commercial distribution system to SMR plant 3) feeding the nominated RNG to a SMR process that uses electricity from the grid along with steam to produce syngas which is then purified to fuel cell quality hydrogen via PSA.

Steam Methane Reforming is widely used today for the production of hydrogen. Syngas production is the process of reacting/combusting a hydrocarbon stream to form hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and water (H_2O). Light hydrocarbons such as natural gas and Refinery Fuel Gas (RFG) and butane are typically used to produce hydrogen. Natural gas and RFG principally consist of methane, ethane, propane, butane, and small quantities of heavy hydrocarbon (C5+), carbon dioxide, nitrogen and sulfur. In Air Liquide’s proposed pathway, some or all of the hydrocarbon feed will be substituted with RNG produced from upgraded waste-derived biogas. The SMR process itself remains unchanged.

Steam Methane Reforming is a catalytic reaction between a hydrocarbon and steam to produce syngas. The hydrocarbon and steam reaction requires heat; therefore, a furnace with burners is required for the reaction to take place. The high temperature syngas effluent stream from the reformer furnace is cooled, producing steam. The cooled syngas stream flows to the shift reactor to produce additional hydrogen and carbon dioxide from any carbon monoxide present in the syngas effluent. The shift reactor effluent is further cooled to condense unreacted steam, allowing it to be recovered for reuse. After the water has been removed, the syngas is purified into hydrogen in a Pressure Swing Adsorption (PSA) unit, with the impurities rejected by the PSA (primarily carbon monoxide, carbon dioxide, and unreacted hydrocarbon feeds) and sent to the furnace as fuel.

If the hydrogen is to be used in industrial applications, the product is sent to the customer via pipeline. If the hydrogen is to be used in the hydrogen fuel cell vehicle market, the product gas will be transported by high pressure tube trailer to hydrogen refueling stations.

Feed Pretreatment

Pretreatment of the hydrocarbon feeds is required to remove sulfur compounds. *[* [redacted] (b) (4) [redacted]

Reforming

(b) (4) [redacted]

[redacted] [redacted] [redacted]

[redacted] [redacted] [redacted]

[redacted]

Shift Conversion

(b) (4) [redacted]

[redacted] [redacted] [redacted]

Process Gas Cooling

(b) (4) [redacted]

Hydrogen Purification

(b) (4) [redacted]

[redacted]

[redacted]

(b) (4) [redacted]*.]*

Heat Recovery/Steam Generation/Power Generation

(b) (4) [redacted]*.]*

Compression/Transport to Fueling Station

(b) (4) [redacted]

2. Mass and Energy Balances

See attachments. **Air Liquide claims all mass and energy balances as CBI**

3. Historical Process Data

4. Information for New Production Processes

i. Energy Saving Technologies or Other Process Improvements

N/A

ii. Request for Special Provisions

N/A

iii. Processes that Use Renewable Fuel Inputs

N/A

5. Other Relevant Information

N/A

E. Feedstock

1. Type of Feedstock

Feedstock is that of Pathway ‘Q’: “Biogas from landfills, municipal wastewater treatment facility digesters, agricultural digesters, and separated MSW digesters; and biogas from the cellulosic components of biomass processed in other waste digesters.”

2. Information for New Feedstocks

N/A

3. Other Relevant Information

N/A

F. Coproducts

1. Technical Description

N/A

2. Market Value

N/A

3. Coproducts Used as Livestock Feed

N/A

G. Attachments

1. Mass and Energy Balance: Biogas-to-Hydrogen Pathway

H. References

[1] Electronic Code of Federal Regulations. <http://www.ecfr.gov/>.

[2] Lower and Higher Heating Values of Fuels. Hydrogen Analysis Resource Center.<http://hydrogen.pnl.gov/tools/lower-and-higher-heating-values-fuels>.

[3] 2015 Annual Evaluation of Fuel Cell Electric Vehicle Deployment and Hydrogen Fuel Station Network Development. California Air Resources Board. <http://www.arb.ca.gov/msprog/zevprog/ab8/ab8_report_2015.pdf>.

[4] Hydrogen Fuel Quality for Fuel Cell Vehicles. SAE International. <http://standards.sae.org/j2719_201109/>.